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Sustainable applications utilizing sulfur, a by-product from oil and gas industry: A state-of-the-art review

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Highlights

- The sulfur market may face a period of oversupply in the near future.
- Review of novel sulfur applications and technologies for a sustainable future.
- Sulfur as a feedstock for industries dealing with scarce resources.

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Abstract

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Abstract

This paper presents a review of current routes to utilize sulfur and sulfuric acid. Sulfur is a by-product from sour gas and crude oil processing and the precursor of sulfuric acid. As an oversupply is projected for the near-term future, it is prudent to investigate new sulfur applications and market domains that may facilitate a balancing of supply and demand. This consideration is especially relevant for the UAE, and the Middle East in general, due to the requirement to develop sulfur-rich sour gas resources to meet increasing energy needs. The goal of this review is to understand current sulfur oversupply, not as a problem, but as an opportunity to

develop more sustainable technologies. Current routes are reviewed, and possible new applications and their potential as a sulfur sink and a sustainable alternative to existing technologies are discussed. Although sulfur is currently in oversupply, less than 5% positive balance according to Harrisson (2016), it must be noted that it is also a critical component in fertilizer production, having a direct impact on the food supply for the world's growing population. Should the world find itself in a sulfur shortage in the future (which could be possible in the long-term (beyond 2030) as a result of growth in renewable energies, shale gas/oil proliferation and population growth), this would be a much greater problem than the current slight oversupply situation, thus making it important to consider sulfur recoverability as a key factor for any sulfur sink technologies explored.

Keywords

Sulfur; Sulfuric acid; Oversupply; Sulfur utilization; Sulfur sustainable technologies; By-product management

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Introduction

Today's sulfur industry is unique compared to other mineral industries – because it is produced primarily as a by-product, sulfur supply and demand are not typically balanced, which has resulted in oversupply over many of the past several years. Nevertheless, sulfur is a valuable commodity and the primary precursor of sulfuric acid, which is considered as an essential chemical for the world economy. The involuntary supply of sulfur can be seen as a chance to develop more sustainable technologies across several industries. This paper reviews possible new applications in the construction, polymer, battery, thermal energy storage, and fertilizer industries, thereby providing the opportunity to more closely balance sulfur supply and demand, for a more sustainable future. Should the world find itself in a sulfur shortage in the future (which could be possible as a result of growth in renewable energy, shale gas/oil proliferation and population growth), this would be a much greater problem than the current slight oversupply situation, thus making it important to consider sulfur recoverability as a key factor for any sulfur sink technologies explored.

Worldwide, elemental sulfur is nowadays nearly exclusively an involuntary by-product of sour gas and crude oil processing to reduce sulfur dioxide emissions from the combustion of said fossil fuels (Ober, 2002). Sour gas contains varying amounts of highly toxic hydrogen sulfide (H_2S) and other sulfuric compounds which are removed by a stripping process, with subsequent conversion of H_2S to elemental sulfur. Crude oil also contains many organic sulfur species, usually in the range of 1 to 3%. When burned, these anthropogenic sulfur emissions contribute to local air pollution, smog, and acid rain. Furthermore, sulfate aerosols increase the planetary albedo by directly or indirectly increasing cloud cover (Stern, 2006). In the troposphere this contributes to climate cooling, slowing down the global warming effect (Eliseev, 2015). This has even led to propositions to use sulfuric acid/SO_2 for geoengineering to mitigate climate change (Eliseev, 2012, Crutzen, 2006).

With increasing demand and depleting oil and gas reserves, more difficult, often sulfur-rich, i.e., “sour” resources are required to be developed, which are less economically attractive than “sweeter” reserves. Dealing with these sour resources is in itself a challenge, but furthermore results in additional involuntary sulfur output, in a currently oversupplied market.

In addition to the exploitation of sourer oil and gas resources, more stringent limits on sulfur levels in fuel are also being implemented worldwide. Therefore, deeper desulfurization is required, which is usually achieved by hydrotreatment, and may further contribute to sulfur oversupply. One example is the new IMO (International Maritime Organization) regulation which will impose a 0.50% sulfur cap (previously 3.5%) on marine fuel from 2020, resulting in the potential for an additional four million tons per annum of elemental sulfur production (approximately 6% of total supply), (Regulation 14 of IMO, 2016). Development of sour gas reserves is the fastest growing source of sulfur, and for the UAE the most important one. Sour gas reservoirs in the Middle East contain varying and considerable quantities of H_2S which must be removed and converted to elemental sulfur in a gas treatment facility, due to its extreme toxicity to minimize environmental emissions. The sour gas is first treated in a gas sweetening unit, where H_2S and CO_2 are removed and concentrated into an “acid gas” stream. This H_2S-rich acid gas is then routed to a sulfur recovery units (SRU) which typically employs the Modified Claus Process (Eow, 2002) for recovery of H_2S as elemental sulfur. In this process, the H_2S is partially oxidized and

subsequentially catalytically converted to sulfur (see Eqs. (1), (2)), which can be transported to market in molten or solid form. Most modern sulfur recovery units employ tail gas treating technologies, downstream of the Claus SRU, which provide sulfur recovery efficiencies in excess of 99.9%.

$$H_2S + 3O_2 \overset{combustion}{\rightarrow} 2SO_2 + 2H_2O$$

$$2H_2S + SO_2 \overset{catalyticstep}{\rightarrow} 3S + 2H_2O$$

An important characteristic of the sulfur industry is the material flow. Most sulfur enters the anthropogenic sulfur cycle by burning fossil fuels directly as atmospheric emissions. Therefore, it doesn't enter the industrial life-cycle of sulfur. Even if sulfur is recovered as elemental sulfur or sulfuric acid, for the most part, after utilization, it is not present in the end product (see Fig. 1).

As can be seen in Fig. 2 the majority of sulfur is converted into sulfuric acid. Only minor amounts of elemental sulfur are directly used for pesticides, agricultural chemicals or other chemical or pharmaceutical application. The sulfuric acid is mostly used as a chemical reagent in leaching or catalytic processes: examples are ore mining or processing of phosphate, petroleum alkylation, manufacture of methyl methacrylate (a precursor for acrylics) and caprolactam (a nylon precursor). At the end of the industrial life cycle, sulfur mainly has to be disposed of as waste, normally by the formation of its salts (sulfates). Most industrial sulfur is released to the environment as either sulfite (e.g. atmospheric emissions) or sulfate (runoff, gypsum) (Rappold and Lackner, 2010)

Fig. 2 illustrates the industrial life-cycle of sulfur from the supply side to the demand side and the final destination. As the most prominent example, and responsible for over 50% of global "sulfur consumption," the production of phosphoric acid depicts the demand-destination situation very well. Sulfuric acid is used as an intermediate in phosphate rock leaching to produce phosphate fertilizer, and sulfur itself ends up as a by-product in the form of phosphogypsum, exceeding more than 200 million tons per year (Sahu et al., 2014). Because of the presence of NORMs (naturally occurring radioactive materials) in many phosphate rock sources, phosphogypsum is usually mildly radioactive, thus being treated as waste and landfilled (Saadaoui et al., 2017) or dumped into the sea (El Gueddar et al., 2015). Examples of the direct use of sulfur are in pesticides, fertilizer

additives, and pharmaceuticals. Several potential new applications will be further discussed in this paper.

Current sulfur and sulfuric acid usage is relatively mature and offers only limited potential to consume the increasing global output (Mohamed, 2006). Therefore, this review will mainly focus on novel technologies, research activities, and sulfur usage that are attractive for regional applications in the Gulf Cooperation Council (GCC) or that may increase global demand in general.

Because of government regulations on allowable sulfur emissions from processing facilities, discontinuing sulfur recovery operations while continuing to process oil and gas is never an option. If a refinery or natural gas operation cannot recover sulfur, for whatever reason, then the operation of that facility must be discontinued, at least temporarily, until the situation has been resolved and sulfur recovery is again possible. Today, most governments worldwide require sulfur recovery units in oil and gas facilities to achieve recovery efficiencies in excess of 99.9%.

Excess sulfur can be stored in granular, pelletized, or molten state. More significant amounts can be stored in blocks, as has been the case in Kazakhstan and Canada (see Fig. 3). Although long-term storage of sulfur in block form can be carried out safely, without negative environmental impact, this type of storage can lead to environmental risks if not implemented with close care and attention (Gosselin et al., 2010). Groundwater can be contaminated due to oxidation of sulfur to sulfuric acid if rainwater runoff is not properly managed (Birkham et al., 2010). Volatile sulfur dust can also be a problem if the structural integrity of the block is not maintained. Tengiz Chevroil (TCO) faced $600 million government fine for storing 10 million ton of sulfur block in 2007, although it is unclear whether this was due to actual environmental impact or whether it was a political issue. In any case, even when implemented properly, sulfur blocking can create negative government/public perception that is difficult for operators to overcome. Canada is one of the few locations in the world where it is an accepted practice, in remote regions where transportation costs are prohibitive.

Rappold and Lackner argue that converting oversupplied sulfur to sulfuric acid followed by chemical neutralization with, e.g., alkaline rocks is the best practice from an environmental standpoint (Rappold and Lackner, 2010). The cost of this sulfur removal could be offset by energy released from the conversion process. The case that sulfur has

to be treated only as a worthless waste product which has to be somehow removed (thereby justifying above strategy) though seems to be a very unlikely scenario in the future.

Due to investment in a dedicated railway (see Fig. 3) and sulfur handling terminals in Ruwais, the UAE's sulfur has excellent access to the world market and therefore could also significantly benefit from a general increase in world consumption. Thus, e.g., in remote locations in Canada or Kazakhstan; however, due to recent efforts to increase in-country value (ICV), the UAE still has a strong interest in producing higher value sulfur products for export to global markets.

The major derivative of sulfur is sulfuric acid (H_2SO_4) which is the world's most widely produced chemical by mass at approximately 240 Million tons per year. The largest single use of sulfuric acid is for the production of phosphoric acid, a precursor to phosphate fertilizers and non-fertilizer phosphates. All traded sulfuric acid comes practically from metals smelters (Europe is the biggest exporter), which produce sulfuric acid as a by-product which must be sent to market. Unlike elemental sulfur, large-scale sulfuric acid stockpiling is cost prohibitive due to the fact that it is liquid at ambient temperature, requiring voluminous tankage for storage of large quantities.

Sulfuric acid is mostly used as a reagent in leaching or catalytic processes, and therefore the sulfur is not consumed and presented in the final product. Either it has to be recycled (petroleum, etc.), or a waste product (gypsum, ammonium sulfate) is created. These waste products can sometimes be marketed, but this largely depends on whether the process by which they were created results in contamination, e.g., NORMs in phosphogypsum. About 10% of global sulfuric acid production is used as a catalyst for gasoline, jet fuel, and polymer production. The acid is not consumed within these processes, but its effectiveness is diminished by contamination with water, hydrocarbons, and other chemicals (King et al., 2013).

The conversion of sulfur into sulfuric acid is a highly exothermic process (see Eqs. (3), (4), (5)). The standard contact process is a net exporter of carbon-neutral heat/electricity. Technology providers are focusing on further increasing the heat recovery potential to use the process in a more effective way to improve economics.

$$S + O_2 \overset{sulfurburning}{\rightarrow} SO_2$$

$$SO_2 + 1/2O_2 \overset{contactprocess}{\leftrightarrow} SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Sulfur is burned at up to 1200 °C. This high temperature is attractive to be used in a Brayton cycle to increase the conversion efficiency from thermal to electricity. As early as 1977, Harman and Williamson (1977) proposed to use a gas turbine for the sulfur burning process (Wojak, 2009). Another option is to externally fire the gas turbines so that the turbine blades are not directly in contact with the highly corrosive exhaust gases (Meher-Homji et al., 2010). The limited market potential though makes it risky to develop this technology further[2].

In 2015 the United Arab Emirates became the largest sulfur exporter worldwide (approximately 6 MM tons per year, which is greater than 10% of global production, retrieved from Global resource trade, 2018, Harrisson, 2016). The main consumers are the fertilizer industry in Morocco, China, and India. However, in recent years, there has been growing concern that sulfur production capacity may exceed the demand from these consumers. This is mainly due to new production dominated by Middle Eastern countries. By 2022, it is estimated that 25–30% of sulfur supply will emanate from the Middle East (Harrisson, 2016).

Currently, the UAE exports more than 95% of its sulfur production to the World market, as illustrated in Fig. 4 with the bold arrow. The biggest consumers are the fertilizer industries in Morocco and China. With increasing demand for energy, and therefore sour gas, it is expected that the UAE's sulfur production will double in the next 10–15 years. This amount of sulfur will be difficult to be absorbed by the market, as the demand for fertilizers is not expected to increase at the same pace. In the next section, different technologies are presented and discussed to avoid stockpiling sulfur, rather than using it as a valuable resource for a sustainable future. However, the current oversupply scenario is not expected to last forever; thus, technologies that will allow recovery of sulfur for future use, when it is needed for fertilizer production, should be given preference.

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Sulfur applications in the fertilizer industry

By far the biggest sulfur consumer is the fertilizer industry, which constitutes approximately 60% of sulfur demand. Fertilizer provides nutrients needed for plant growth and development. These nutrients can be divided into primary nutrients NPK (nitrogen, phosphorous, and potassium) and secondary nutrients (calcium, magnesium, and sulfur).

Although sulfur is an essential plant nutrient, most sulfur is consumed in the form of sulfuric acid to produce phosphoric acid and subsequentially …

Conclusion

Sulfur is primarily produced as a by-product of fossil fuel utilization because sulfur components must be removed from raw hydrocarbons. This is to minimize SO_2 emissions to the atmosphere which contribute to acid rain. Most oil and gas producers view sulfur as an unwanted by-product and strictly a cost of production. However, this essential element actually has a very robust value chain of its own, with most being converted to sulfuric acid - the world's most widely produced chemical. Because …

Acknowledgments

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